Saskatchewan
Research Council

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THE RAIN CHEMISTRY OF SASKATCHEWAN

by

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ABSTRACT

For several years the Saskatchewan Research Council has studied the rain chemistry of Saskatchewan. Two major networks have been set up in the northern and southern areas of the province. The wet deposited sulphate in the rain from the northern network was in the order of 1.5 kg/ha for the period of study. In the southern network the wet deposited sulphate ranged from 1.3 to 1.7 kg/ha again for the period of the study. The precipitation of Saskatchewan is acidic with volume weighted mean pH values for the northern and southern areas being 5.4 and 5.1 respectively. There was a small increase in the alkaline earth structure of the rain in the southern part of the province.

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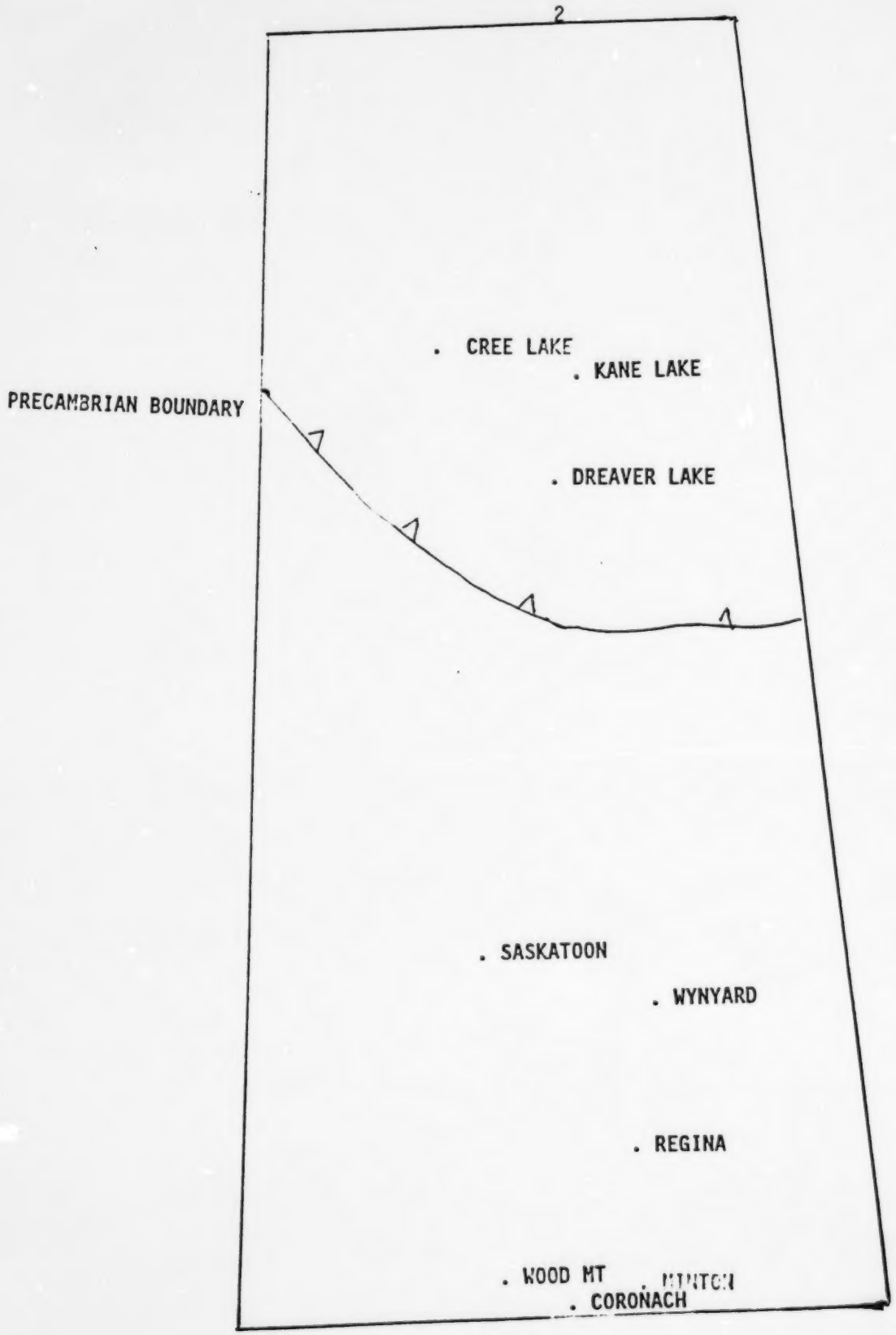
1 INTRODUCTION

It is no longer acceptable to consider the pH of precipitation at remote locations as controlled primarily by carbon dioxide (pH value of 5.6). Natural sources of sulphur and nitrogen species, organic acids, etc. lead to a background level of acidity in the atmosphere. This shows up in precipitation as a pH of approximately 5.0 plus a large standard deviation depending on the amount of incorporated alkaline dust from the surface of the earth. Charlson and Rodhe (1982) have suggested that trace levels of SO_2 may indeed be responsible for the background acidity of rain. Keene et al. (1982) also estimates the level of acidity at remote points to be approximately 5.0. They base this estimate, in part, on trace levels of naturally occurring acids, such as, acetic and formic acid.

The Atmospheric Environment Service (AES) long range transport model was applied to selected locations in western Canada to assess its ability to estimate sulphate deposition from various sources in western North America (Kociuba et al 1984). The model revealed near background wet deposition of sulphate at remote sites.

The rain chemistry of Saskatchewan was studied with two separate networks (Figure 1). There was a northern and a southern network. The northern network was located in the Precambrian Shield and the southern network was located in the agricultual areas to the south. The northern network was established by Saskatchewan Environment. It is described in detail in Shewchuk (1985). The southern network was established by the Saskatchewan Research Council (SRC) for the Saskatchewan Power Corporation. It is described in detail in Shewchuk (1984). In each region the rain was collected by event collection procedures.

Figure 1. THE LOCATION OF RAIN COLLECTION SITES IN SASKATCHEWAN



2 PROCEDURES

The northern Saskatchewan collector is seen in Figure 2. It is a manually operated unit that is opened at the beginning and closed at the end of rainfall. An event was defined as the time periods during which the precipitation occurred. Immediately after the event occurred the sample was collected and preserved for transport to the analytical laboratory. The sample was preserved by freezing. The southern area collector was a Saskatchewan Research Council (SRC) designed bucket (Figure 3) (see Appendix for more detials). The SRC unit was fully automated. After the rain sample had been collected it was frozen immediately in precleaned vessels. The samples were then transported to the analytical laboratory on a monthly basis. All samples from the northern and southern areas were analysed at the end of the field year at the SRC laboratories by the same technicians.

The analytes of primary concern were sulphate, nitrate, hydrogen ions and various metals. The analytic techniques used are shown in Table 1.

Figure 2. The Saskatchewan Environment rain collection bucket from the north.

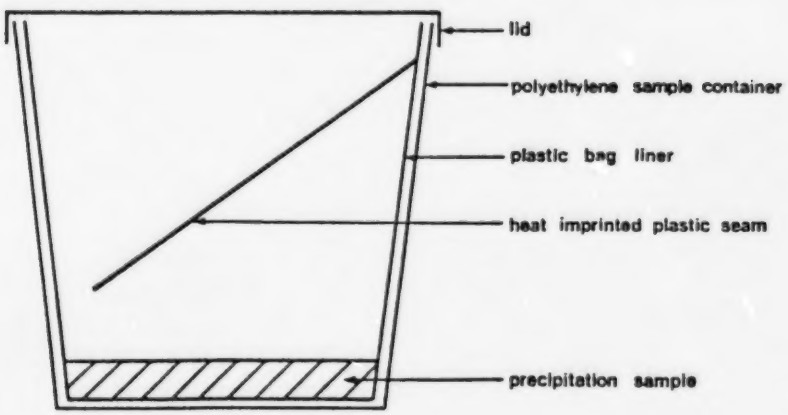


Figure 3. The SRC collection rain collection bucket used in the south.

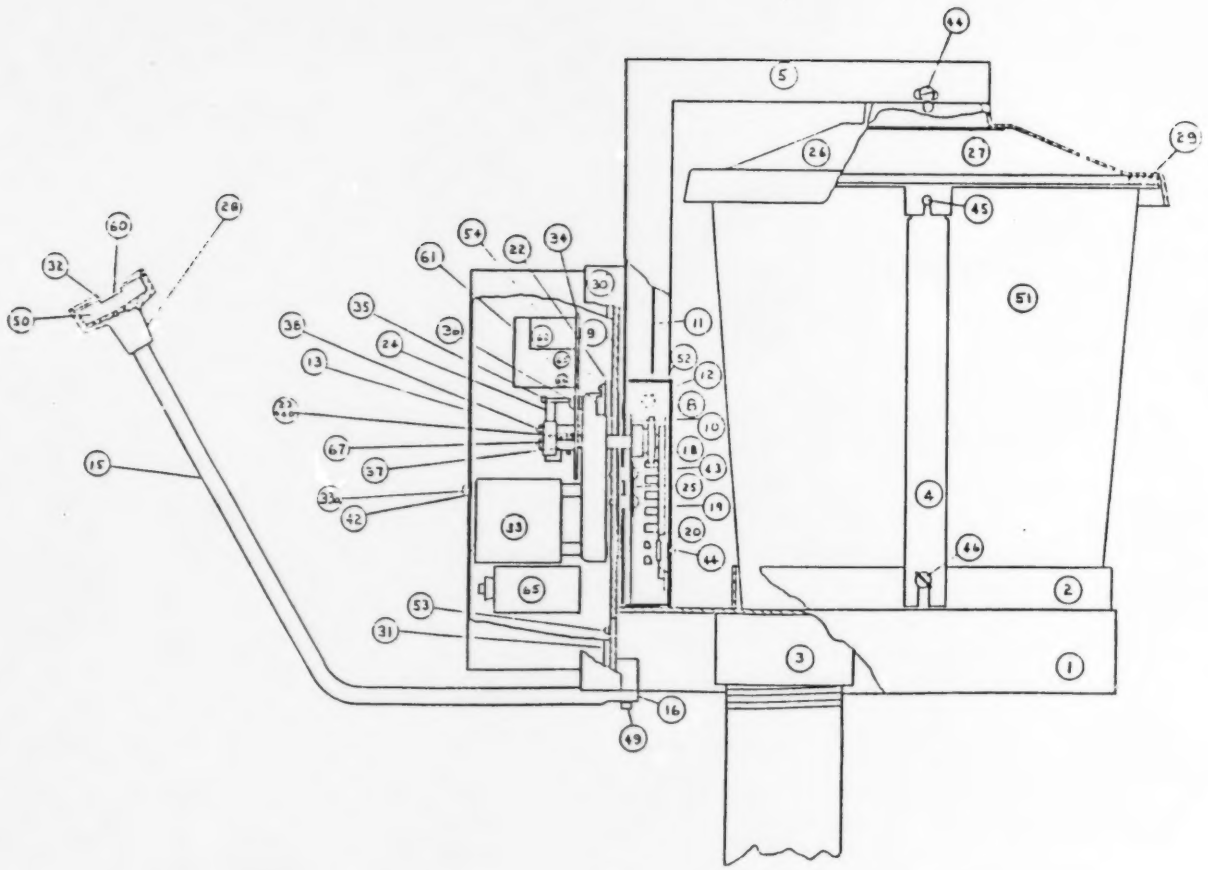


TABLE 1. ANALYTICAL TECHNIQUES USED FOR THE RAIN CHEMISTRY.

ANALYTE	METHOD
SULPHATE	ION CHROMATOGRAPHY
NITRATE	CADMIUM REDUCTION
pH	TITRATION
AMMONIA	TITRATION
VARIOUS METALS*	ICP (INDUCTIVELY COUPLED PLASMA SPECTROMETRY)

*INCLUDING (Ca, Na, K, etc.)

3 RESULTS

The results from the northern network are shown in Table 2. There are two locations reported here out of a five collector network. The volume weighted mean values are calculated by multiplying the individual rainfall concentration by the amount of rain that fell in each event and dividing by the total amount of rainfall in the period from May 1 to October 31, 1983. Volume weighted concentration, wet deposition and estimated annual deposition is seen in this table for sulphate, nitrate and calcium.

The results from the southern network are shown in Table 3. There are two locations reported out of a six rain collector network. Similar parameters are seen in this table.

Table 4 shows the pH range for the rain chemistry collected in the northern and southern networks. The rain can be considered acidic in both areas of the province. In addition there is a comparison to the volume weighted mean pH values of 1980 as given for this area of Canada in the Memorandum of Intent (MOI) (Bangay and Riordan 1983). It is seen that the rain of southern Saskatchewan is considerably more dilute than indicated by the 1980 observations.

Table 5 is a comparison between the estimated annual sulphate deposition from this paper and the AES western region model. It is seen that sulphate deposition for the north from the Saskatchewan Environment network is significantly less than estimated by the AES model. On the other hand, there is quite good agreement between the AES model and the SRC network from the southern part of Saskatchewan.

Table 6 is the annual depositions of sulphate and nitrate for Sas-

katchewan as given in the MOI. Northern Saskatchewan is represented by Cree Lake and southern Saskatchewan is represented by Wynyard. Values reported in this document are considerably higher in total deposition than estimated in this program. One possible reason for the discrepancy could be due to the fact that the SRC network in both the regions did not measure deposition directly in the winter months. It is important to recall that the SRC network was a purely event network (i.e., the sample was collected immediately after ending of the precipitation activity). In addition the collector used in the south was designed to have a tight mechanical seal when not collecting precipitation.

TABLE 2. NORTHERN SASKATCHEWAN RAIN CHEMISTRY, 1983.

A) VOLUME WEIGHTED MEANS

LOCATION	SO_4 (mg/L)	NO_3 (mg/L)	Ca (mg/L)
DREAVER	0.63	0.49	0.32
KANE	0.49	0.31	0.14

B) DEPOSITION (MAY 1 TO OCTOBER 31)

LOCATION	AMOUNT (mm)	SO_4 (kg/ha)	NO_3 (kg/ha)	Ca (kg/ha)
DREAVER	247.8	1.55	1.24	0.79
KANE	302.5	1.47	0.89	0.41

C) ESTIMATED ANNUAL WET DEPOSITION (BASED ON 375.7 mm TOTAL PRECIPITATION)

LOCATION	SO_4 (kg/ha)	NO_3 (kg/ha)	Ca (kg/ha)
DREAVER	2.35	1.86	1.20
KANE	1.83	1.11	0.51

TABLE 3. SOUTHERN SASKATCHEWAN RAIN CHEMISTRY, 1984.

A) VOLUME WEIGHTED MEANS

LOCATION	SO_4 (mg/L)	NO_3 (mg/L)	Ca (mg/L)
WOOD MOUNTAIN	1.30	0.80	0.57
CORONACH	1.78	1.10	0.48

B) DEPOSITION (JUNE 1 TO SEPTEMBER 31)

LOCATION	AMOUNT (mm)	SO_4 (kg/ha)	NO_3 (kg/ha)	Ca (kg/ha)
WOOD MOUNTAIN	103.0	1.34	0.82	0.58
CORONACH	93.5	1.66	1.02	0.45

C) ESTIMATED ANNUAL WET DEPOSITION (BASED ON 380 mm TOTAL PRECIPITATION)

LOCATION	SO_4 (kg/ha)	NO_3 (kg/ha)	Ca (kg/ha)
WOOD MOUNTAIN	4.94	3.04	2.14
CORONACH	6.75	4.15	1.83

TABLE 4. THE pH RANGE FOR RAIN IN SASKATCHEWAN.

LOCATION	VOLUME WEIGHT MEAN pH	RANGE	VOLUME WEIGHTED MEAN pH 1980 (MOI)
NORTH	5.4	4.8 - 6.5	5.2
SOUTH	5.1	5.0 - 5.8	6.5

TABLE 5. ANNUAL SULPHATE (SO_4) DEPOSITION ESTIMATED IN kg/ha FROM THIS PAPER AND THE AES MODEL OF SULPHUR DEPOSITION (Kociuba et al 1984).

LOCATION	SRC	AES
NORTH	2.4	3.9
SOUTH	4.9	4.2

TABLE 6. ANNUAL DEPOSITION IN SASKATCHEWAN AS GIVEN IN THE MEMORANDUM OF INTENT, 1980.

LOCATION	SO_4 (kg/ha)	NO_3 (kg/ha)
NORTHERN SASKATCHEWAN	4.90	2.17
SOUTHERN SASKATCHEWAN	11.5	12.4

4 DISCUSSION

The rain in both areas of Saskatchewan is acidic. On an annual basis the deposition of both calcium and sulphate is marginally higher in the southern regions. The volume weighted mean sulphate, nitrate, and calcium concentrations are approximately a factor of 2 higher in the south than in the north. According to the measurements of volume weighted pH the rain is significantly less alkaline than considered by MOI 1980 value for southern Saskatchewan.

The annual sulphate and nitrate deposition as given in the MOI 1980 report is significantly higher than reported in this work. It is felt that this is cause for some concern in understanding the rain chemistry of Saskatchewan. One possible explanation for the high sulphate loadings from the MOI values could have been the monthly integrated sample approach. This research put great emphasis on the collection of precipitation by event sampling procedures, where the event was defined as the duration of rainfall. It is interesting to note that the SRC southern Saskatchewan network agrees quite well with the AES model results of Kociuba et al (1984).

The lack of agreement in the north between the SRC analyzed results and the AES collected and modelled results is cause for some concern. There is logically no apparent reason for the lack of agreement of these networks. The area of northern Saskatchewan is located on the Precambrian Shield formation of Canada. The region is characterized by little alkaline dust in the atmosphere and low rainfall amounts. It is recommended that AES, SRC and Saskatchewan Environment confer as to reasons for the discrepancies.

In summary in ion chemistry the SRC network is more dilute than that previously reported. It is unlikely that reasons for difference occur in the laboratory analysis because samples would likely be biased high due to contamination. Any differences are most likely due to collection or sample handling procedures. It is felt that the SRC southern Saskatchewan data is representative of the region. Values of wet deposition for the north deserve more attention.

5 REFERENCES

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7. APPENDIX

THE SRC RAIN COLLECTOR

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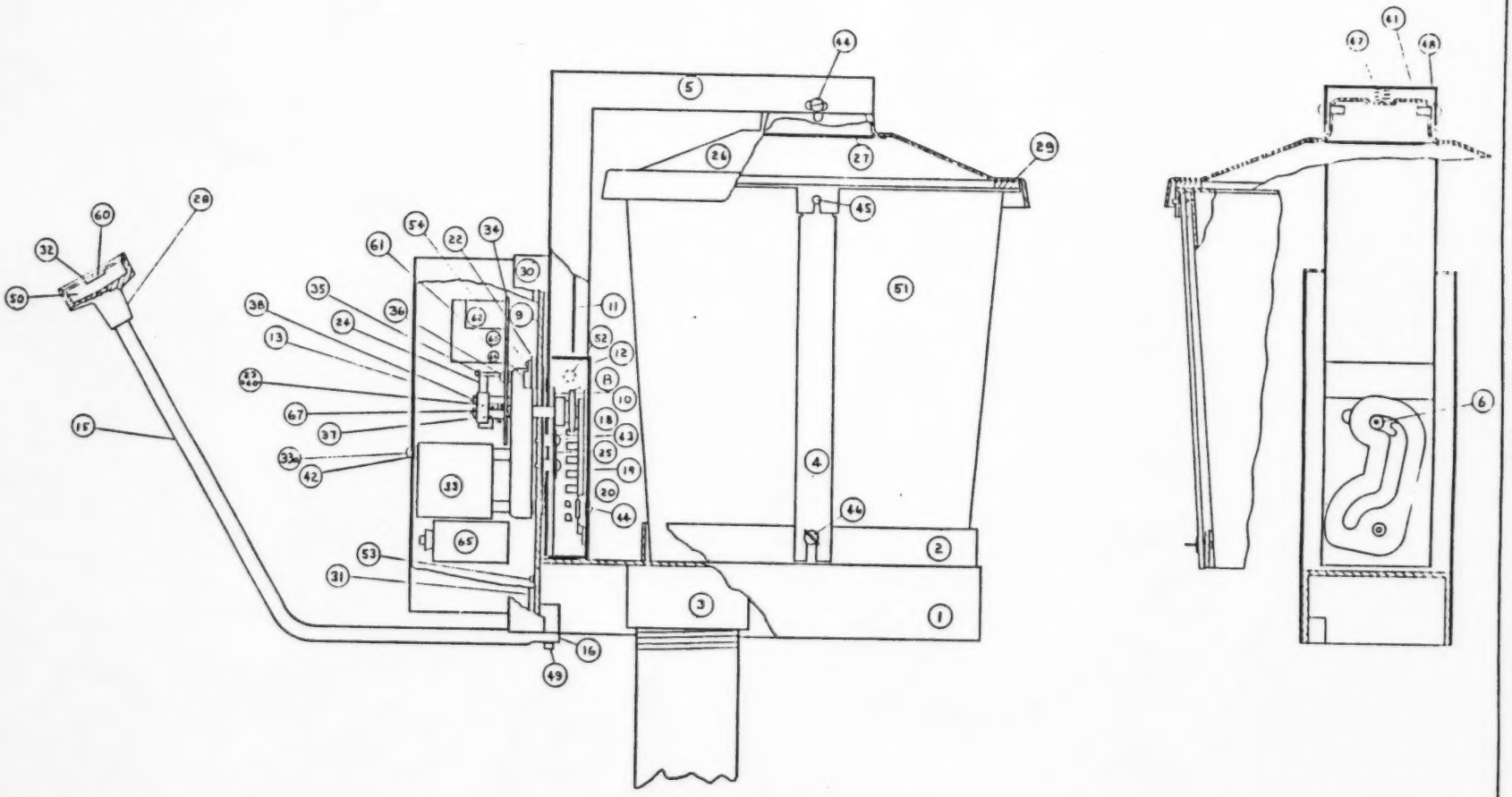
AUTOMATED PRECIPITATION COLLECTOR

(This unit is for commercial sale)



CANADIAN CENTRE FOR ADVANCED INSTRUMENTATION		
SCALE	APPROVED BY CJD	DRAWN BY A.T.P
DATE MAY 1984		REVISED
ACID PRECIPITATION COLLECTOR		
		DRAWING NUMBER APC-10

The C.C.A.I. Acid Precipitation Collector is designed to collect liquid and frozen precipitation and maintain the sample in as pure as collected form as possible. It does this by employing a covered collector which automatically opens upon the start of precipitation and closes immediately after the event. The accumulated sample may then be taken from the collector and analysed for contaminants.

The C.C.A.I. Collector is unique in three areas:

a) It has a simple, trouble free, lid moving mechanism which locks upon closing to ensure a positive seal on the Collector.

b) It uses a simple and efficient precipitation sensor which is heated by a novel application of a disc thermistor and functions both as a temperature sensor and a heater.

c) The lid rotates to the side in such a way as to minimize splashing.

Operating Principle

Mechanics -

The lid is actuated by a gear-head motor through a sprocket and a specially designed sprocket cam follower which provides the three required conditions, namely: lock, lift and rotate. The moulded A.B.S. lid is sprung and fully articulated so as to align itself on the collector and provide equal force on all areas of the lid gasket.

Electrical -

110V AC power is applied through a 1 amp fuse to the power transformer T-1. There are two 10 VAC outputs, one is rectified by BR-2 and filtered by C-2 to provide approximately 12V DC to the relay circuit and

the sensor heater circuit. The other is rectified by BR-1 and applied through R6 and the sensor grid (when wet) to quickly charge C-1 and turn on Q1, which causes the relay to pull in. This applies AC power to the gearhead motor which opens the lid. The motor is switched off by limit switch SW-2.

Sensor heater current is supplied by voltage regulator LM317 which along with R-2, functions as a constant current source. When the lid is closed, this current is .22 amps. When the relay pulls in and the lid opens, a set of contacts in the relay close, connecting R-5 in parallel with R-2 and causing the output current to rise to approximately .45 amps. This current boost accelerates the drying action of the sensor. When the sensor dries and its impedance rises to a high value, the charge on C-1 leaks to ground through R-1. After a delay of approximately 100 seconds, Q-1 turns off and the relay drops out. This causes the motor to close and lock the lid. Limit switch SW-1 then stops the motor. The sensor heater current also drops back to .22 amps.

Sensor Heater -

The sensor employs a large disc thermistor thermally attached to its underside. The thermistor's negative temperature coefficient of resistance coupled with a constant current source causes the thermistor to automatically adjust its power dissipation with respect to ambient temperature. A Fenwal MB13J1M thermistor, with a dissipation constant determined by the sensor-thermistor thermal coupling and a constant current of .22 amps provides a sensor surface temperature, in still air, as follows:

- when the ambient is +40°C, the sensor surface temperature is +47°C
- when the ambient is -40°C, the sensor surface temperature is 0°C

Installation

Mount the collector by screwing it onto a threaded (MPT) 2½" steel or aluminum pipe, securely fastened to the ground. Supply the collector with 110 VAC 60HZ power via an armoured #14 x 2 + ground cable which is wired to the mains through a 15 amp breaker. This breaker will act as an on-off switch. Remove the electronics cover by screwing the two exposed screws CCW until the cover comes free. Feed the electrical cable through a suitable ½" connector installed in the hole in the lower back plane. Connect the ground wire to the screw on the left side of the connector. Dress and connect the two power wires to the pig-tails with the twist-on connectors supplied. Tuck the wires out of the way of any mechanism and replace the cover and turn on the breaker.

- To open the collector, simply apply a few drops of water to the sensor grid. This will keep the cover off for 4 to 6 minutes, until the water evaporates, allowing one to remove the sample or check the Collectors operation.